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MOLECULAR BEAM STUDIES OF SULFUR HEXAFLUORIDE CLUSTERING IN AN ARGON CARRIER GAS FROM BOTH FREE JET AND LAVAL NOZZLE SOURCES

by

Barry G. DeBoer Sang Soo Kim, and Gilbert D. Stein

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NORTHWESTERN UNIVERSITY

Department of Mechanical Engineering
and Astronautical Sciences

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Experiments on adiabatic expansions of SF_6 in an argon carrier gas reveal that it readily nucleates and grows in the small free jets and Laval nozzles used as molecular beam sources. One free jet orifice and one nozzle of approximately the same throat size were used in this work. Limits for the onset of clustering leading to intense "molecular" beams have been determined by varying the initial pressure, initial temperature, SF_6 mole fraction and gas expansion (and cooling) rate. As anticipated, the Laval nozzle is a much more efficient cluster generator than the

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Barry G. DeBoer, Sang Soo Kim, and Gilbert D. Stein

Gasdynamics Laboratory
Department of Mechanical Engineering
and Astronautical Sciences
Northwestern University
Evanston, Illinois 60201 USA

ABSTRACT

Experiments on adiabatic expansions of SF_6 in an argon carrier gas reveal that it readily nucleates and grows in the small free jets and Laval nozzles used as molecular beam sources. One free jet orifice and one nozzle of approximately the same throat size were used in this work. Limits for the onset of clustering leading to intense "molecular" beams have been determined by varying the initial pressure, initial temperature, SF_6 mole fraction and gas expansion (and cooling) rate. As anticipated, the Laval nozzle is a much more efficient cluster generator than the free jet. High energy electron diffraction has been employed to ascertain the cluster size, crystalline structure (body centered cubic), and unit cell dimensions as functions of the initial conditions. Estimates of the cluster temperatures have been made from their cell dimensions.

INTRODUCTION

Sulfur hexafluoride clustering in molecular beams has been investigated in our laboratory partly because of current interest in gas phase and beam isotope separation schemes using UF_6. As is frequently the case, the limits of clustering and nucleation are required in order to avoid these phenomena in the isotope separation processes. We also have continuing interests in both the structure and properties of small clusters as well as the initiation of the phase change process. In order to produce clusters of low-γ molecules (i.e. γ, the ratio of specific heats, approaching 1) a high-γ carrier gas is required to provide the undercooling necessary for a significant amount of clustering to ensue. Argon ($\gamma = 5/3$) was used as the carrier gas. Light scattering studies of SF_6 nucleation in argon expansions in a Laval nozzle have recently been reported.[1] Expansions in a high-γ carrier gas have been shown to produce more intense beams of smaller clusters from both nozzles and

free jets[2], and are expected to produce narrower size distributions and lower cluster temperatures than pure gas expansions[3-4]. All of these features are desirable for cluster structure studies using electron diffraction.

Our experimental technique uses the now-standard, three-stage molecular beam apparatus; a nozzle, skimmer, and collimator with an ionization gage as a beam detector. Immediately behind the collimator, the molecular beam is crossed by a 40 kev electron beam and cluster diffraction patterns are recorded on photographic plates in a rotating-sector camera[5-7]. The limits of SF_6 clustering were studied as a function of stagnation pressure, temperature, and SF_6 mole fraction, P_o, T_o, χ_{SF_6}. Additional gasdynamic measurements on the Laval nozzle were conducted in a separate apparatus to determine the variation in thermodynamic properties through the nozzle for a variety of operating conditions. The clusters formed in the free jet and nozzle expansions were examined using high energy electron diffraction to determine their structure, sizes, and unit cell dimensions, the latter interpreted as measuring the cluster temperature.

FREE JET MOLECULAR BEAM

Free-jet gasdynamics are well known and fully documented and thus need not be reproduced here (many references appear in earlier volumes of these Proceedings). The experimental parameters were systematically varied to determine the conditions required for the onset of nucleation. Figure 1 shows an "iso-intensity" plot of the free jet cluster beam as a function of the partial pressures of SF_6 and Ar. As in past work, a rapid increase in intensity is evidence for massive clustering[8-9]. It is seen that the locus of onsets forms the base of a steeply rising intensity hill. These intensity contours were mapped out at $T_o \simeq 294$K and a constant nozzle-to-skimmer distance of 0.75 cm found by seeking the maximum beam intensity. The skimmer had a diameter $D_s = 0.094$ cm and collimator $D_c = 0.208$ cm. The SF_6 mole fraction was varied by mixing a fixed, choked flow of SF_6 with a variable argon flow. There appears to be a limiting mole fraction (about 0.4) above which there are no onsets. This is believed to be due to the lowering of γ with increasing SF_6 mole fraction which raises the temperatures throughout the expansion such that there is no significant nucleation of SF_6. This effect is clearly seen in much larger Laval nozzles[1].

A MACH 6 TO 8 NOZZLE SOURCE

Using premixes of χ_{SF_6} equal to 0.03, 0.0625, and 0.125 a partial intensity map for the small Laval nozzle source is shown in Fig. 2. This nozzle was drawn from glass tubing. Its measured contour was least-squares fit to the polynomial:

$$D(x) = 0.0125 - 0.0394x + 1.004x^2 - 2.981x^3 + 4.026x^4 - 0.6153x^5 - 2.480x^6 + 1.277x^7, \quad (1)$$

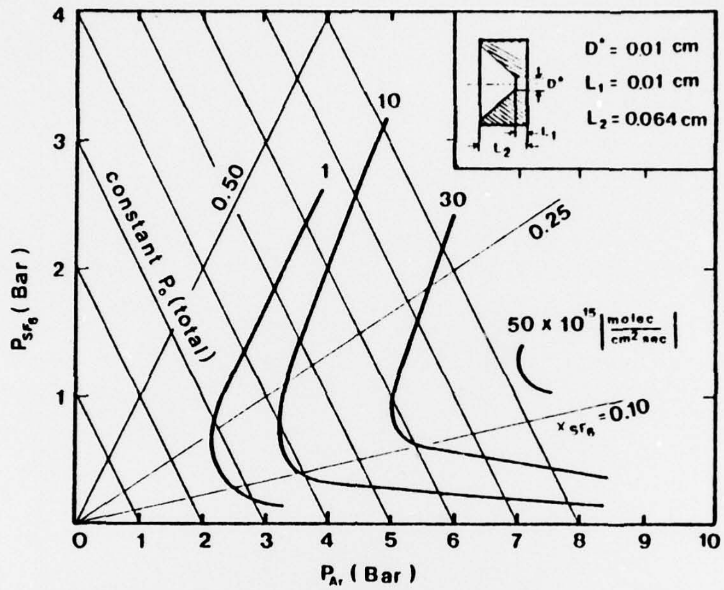

Fig. 1. Molecular beam intensity contours as a function of the partial pressures of Ar and SF_6 for a free jet source at $T_o \simeq 295$ K and at the electron beam about 7cm from the free jet orifice.

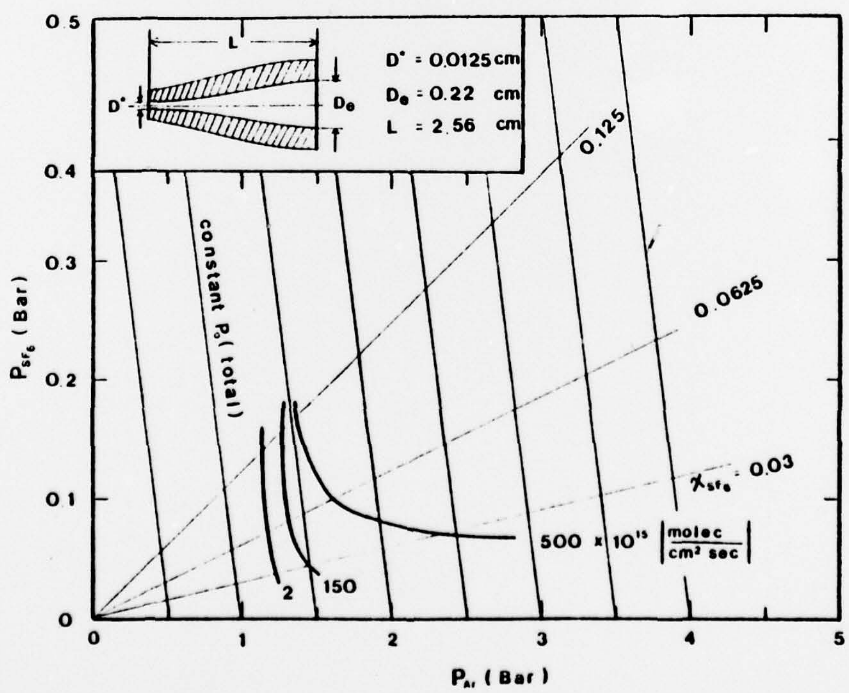

Fig. 2 Molecular beam intensity contours for a nozzle of nearly the same throat diameter as free jet of Fig. 1.

where D and x are both in centimeters.

Exit Mach numbers for this nozzle seen in Fig. 3 for argon, helium, and 6.25% SF_6 in argon are based on static pressure measurements at the nozzle exit, the assumption of a one-dimensional flow with an isentropic core and, for the SF_6 mixture, a constant $\gamma = 1.485$. Mach numbers plotted represent upper limits. The exit Mach number M_e increases with P_o because of decreasing boundary layer thickness. As expected, boundary layers are thicker for helium than for argon.

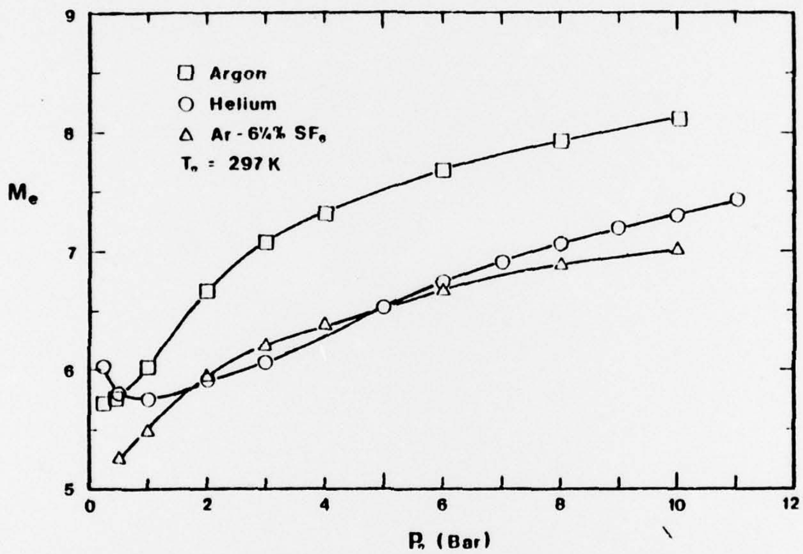

Fig. 3 The nozzle exit Mach number M_e is plotted as a function of P_o based on static pressure measurements at the exit and the assumptions described in text.

BEAM INTENSITIES

Results of experiments on 3% SF_6 in argon are displayed in Figs. 4 and 5. The cluster beam flux I_B (no./sec) has been "normalized" by the total beam source SF_6 flow rate $\dot{N}_{SF_6}$. The beam flux I_B is virtually all SF_6 (in clusters) since pure argon expansions at these pressures have negligible intensities. The onset of massive clustering in the nozzle occurs at lower pressure for the 6.25% mixture than for the 3%. This is due to the higher initial vapor pressure of the 6.25% mixture, but it is not linear with pressure (i.e. $P_o(3\%) \neq 2P_o(6.25\%)$). From 6.25% to 12.5% the onset trend reverses and $P_o(12.5\%) >$ P_o (6.25%). Even though the mole fraction increased, the reduction in the heat capacity ratio $\gamma = c_p/c_v$ dominates, requiring a higher P_o to restore the necessary supersaturation. This γ effect is also the reason for the non-linear relation between the 3% and 6.25% mixtures seen above. That the normalized beam intensity reaches a plateau strongly suggests that effectively all of the SF_6 in the mixture has condensed. We also observe

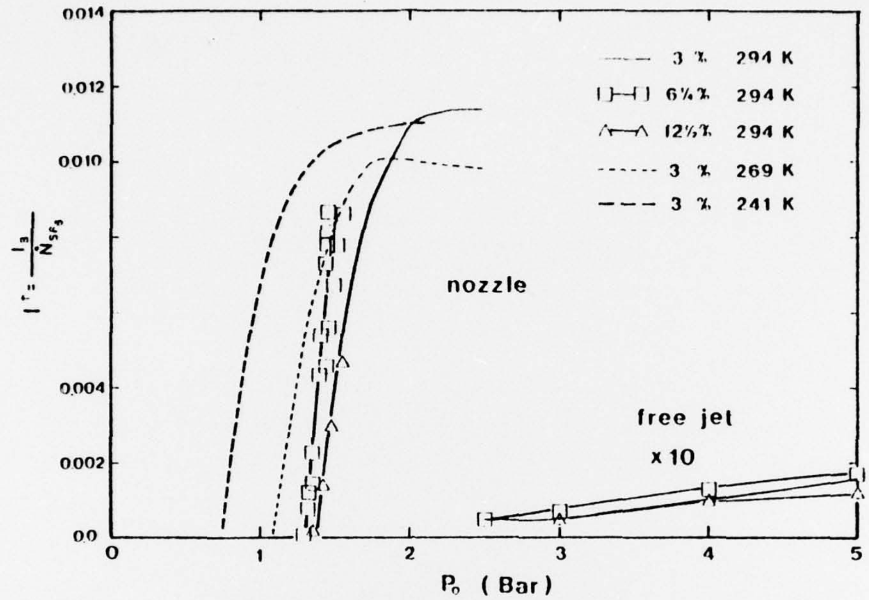

Fig. 4 The molecular beam flux I_B, "normalized" by the total SF_6 flow rate through the source $\dot{N}_{SF_6}$, and plotted as a function of P_o. The 6.25% and 12.5% curves terminate where they exceed our detector's range; the 12.5% curve overlays part of the 3% curve.

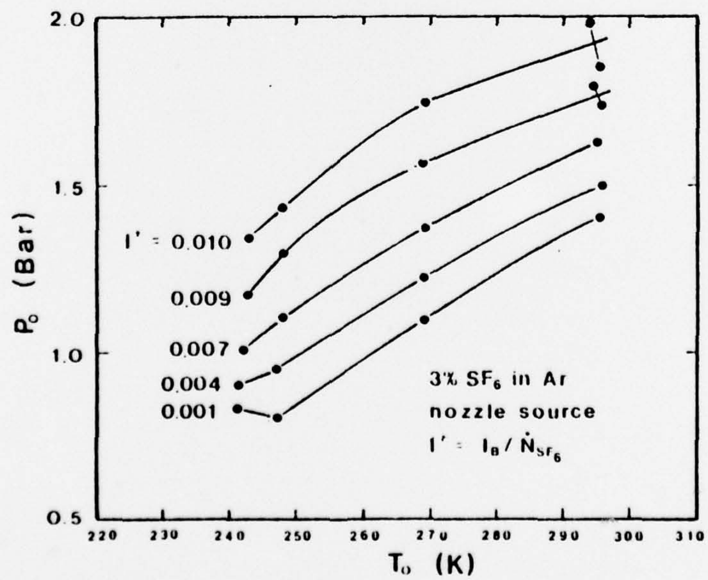

Fig. 5 An Iso-intensity plot for the 3% mixture as a function of P_o and T_o results in a nearly linear profile.

the expected monotonic variation (at constant γ) of the onset pressure with temperature, T_o, in the three nozzle 3% SF_6 curves. These colder expansions come to the same normalized beam intensity limit. These relations are more clearly displayed in Fig. 5.

The final feature to be seen in Figure 4 is the drastically lower intensity of the free jet expansion. As expected from prior research[2], a nozzle, which controls the rate of expansion, is a much more efficient cluster generator. That is, the nozzle can produce a cluster beam of a given intensity with a much smaller gas load on the pumping system.

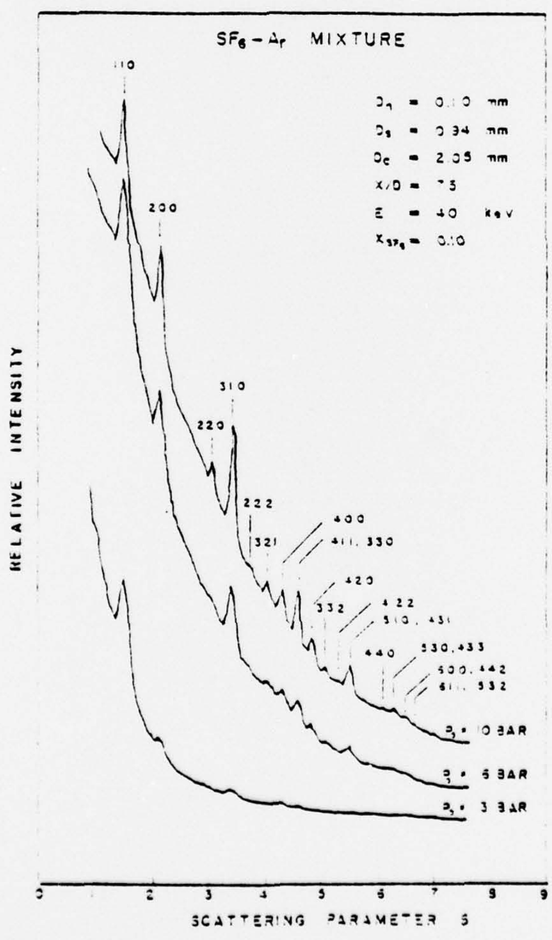

Fig. 6 A series of electron diffraction patterns for the free jet source at $T_o \cong 245$ K and an SF_6 mole fraction of 0.1. The scattering parameter is $s = (4\pi/\lambda)\sin(\theta/2)$ where λ is the electron de Broglie wavelength and θ is the scattering angle. The Miller indices are assigned for a BCC unit cell.

CLUSTER ELECTRON DIFFRACTION

The scattering of high energy electrons (40 kev) from the cluster beam gives rise to Debye-Scherrer diffraction patterns[5-7]. Typical patterns for the free jet source are presented in Fig. 6 and provide evidence that there are indeed clusters in the beam when the ionization gage registers high beam intensity, and that the clusters are crystalline, not amorphous solid or liquid[7]. Secondly, for large cluster sizes, the patterns are consistent only with a simple body-centered cubic (BCC) crystal structure, with two SF_6 molecules per unit cell [space group Im3m(O_h^9, No.229), S in position 2a, F in 12e][10,11].

The average crystallite size d, is determined by

$$d = K\lambda/\beta \cos\theta \simeq L\lambda/(W^2 - W_o^2)^{\frac{1}{2}} \quad (\theta \ll 1) \quad , \qquad (2)$$

where λ is the electron wavelength, K is a shape factor ($K \simeq 1.0$), θ is the Bragg angle, β is the true line broadening in radians, L is the sample-to-plate distance and W and W_o are the line-widths for the sample and the reference (Au thin film, presumed to be composed of "large" crystallites) materials, respectively. The average width of the 110,200, and 310 peaks were used to estimate d values which are identified with the cluster diameter. The unit cell dimension, a, is determined from the peak locations in the usual way using the BCC indexing shown and a camera constant ($L\lambda$) obtained from a gold thin film standard. Crystallite size, d, and cell dimension, a, data are presented in Fig. 7 as a function of initial total pressure P_o. The average "cluster" size is seen to go through a maximum for the 3% and 6.25% mixtures. There is no known feature of the nozzle expansion, nucleation, and growth that could explain the apparent decrease in cluster size with increasing P_o. That the clusters might be being destroyed by denser background gas and shocks at higher P_o's is contradicted[12] by their lower temperatures (see below). We favor the explanation that the clusters become polycrystalline (or are badly distorted)[12] at higher P_o, where the higher densities throughout the expansion lead to both higher condensation rates and faster cooling of the clusters once they are formed, creating and then freezing in the disorder indicated by the small d values. Evidence for disorder in clusters is presented elsewhere[13] in these Proceedings.

The unit cell dimension, a, decreases with increasing P_o in all cases. It is known to decrease with decreasing cluster size[14-16] and with falling temperature[17,18]. The cluster-size dependence is not seen here since a seems uncorrelated with d, and if the true cluster size increases with P_o, then the cell dimension variation has the wrong sign. On the other hand, the cluster temperature is expected to decrease with increasing P_o, for fixed SF_6 mole fraction due to the increased number of collisions that a cluster has with the argon carrier gas after it has stopped growing because of the depletion of the SF_6

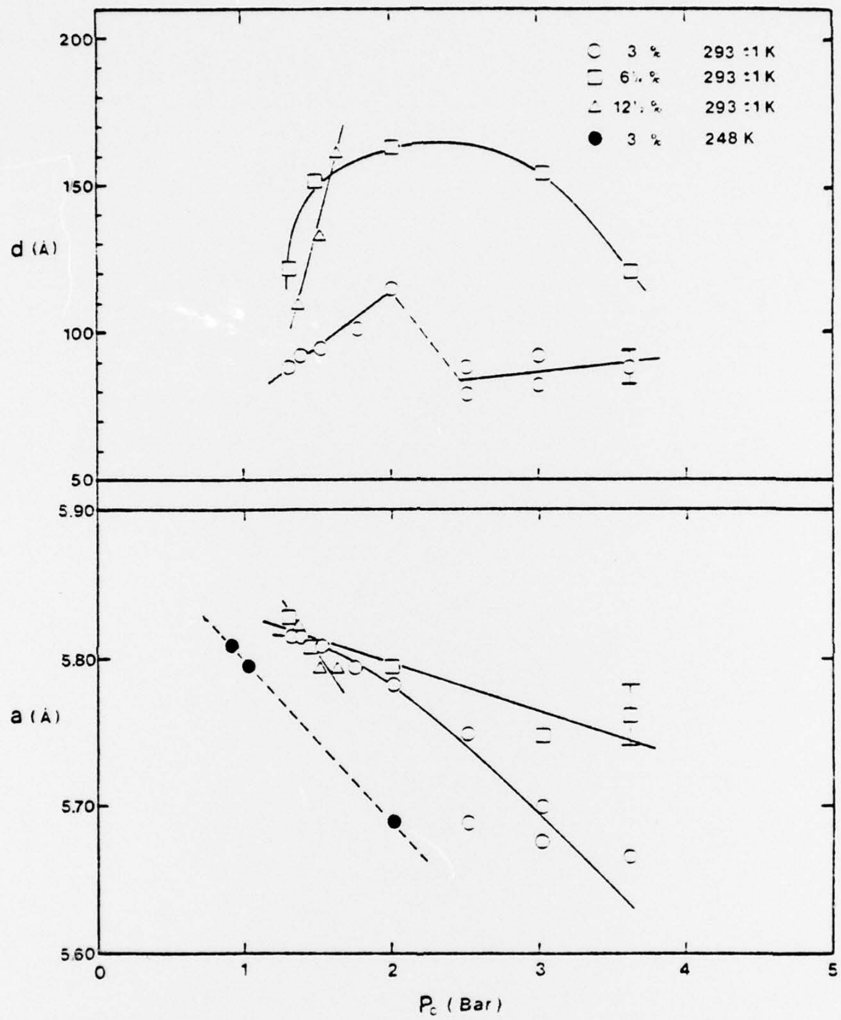

Fig. 7 Average SF_6 crystallite sizes and unit cell dimensions from electron diffraction patterns taken with the nozzle source and premixed 3%, 6.25% and 12.5% SF_6 in Ar.

supply (see Fig. 4). Finally, it is seen that decreasing T_o at any given P_o, which is expected to lower the final cluster temperature does give smaller unit cell parameters.

On this basis, the unit cell dimension can be used as a measure of the cluster temperature, provided that a calibration can be found. A value of a = 5.79 ± .01 Å at 123K has been reported[19] for SF_6 together with a linear expansion coefficient of 3.6×10^{-4} deg^{-1} for the similar (one hopes) selenium hexafluoride. These values applied to the 5.82Å - 5.66Å range of a, indicates cluster temperatures from 137K to 61K. Alternatively, the measured[20] density of solid SF_6, 2.683 g/cc at 78K can be

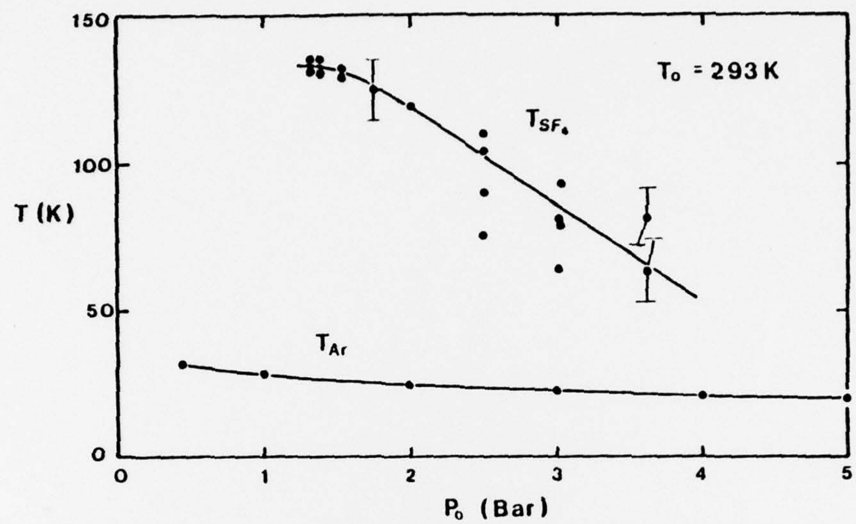

Fig. 8 Estimated temperatures of the SF_6 clusters and of the argon carrier gas as a function of P_0 for the 3% premixture expansion through the nozzle source.

converted, knowing the molecular mass and Avrogadro's number, to a = 5.654 Å. These two cell dimensions give an expansion coefficient of 3.0×10^{-4} deg^{-1} and a cluster temperature range of 133K - 81K. These estimates of cluster temperature are displayed in Fig. 8 together with argon carrier gas temperatures estimated from the data of Fig. 3. Note that the temperature difference is large, as seen previously[16,21], but decreases with increasing P_0.

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